

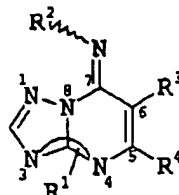
Fungicidal Triazolopyrimid-7-ylideneamines

Description

5

The present invention provides compounds of formula I

10



I

in which

15 R^1 is C_1 - C_{10} -alkyl, C_1 - C_6 -alkoxy- C_1 - C_6 -alkyl, C_3 - C_8 -cycloalkyl- C_1 - C_6 -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, C_4 - C_{10} -alkadienyl, C_1 - C_{10} -haloalkyl, trihydrocarbylsilyl, formyl, C_1 - C_{10} -alkanoyl or C_1 - C_{10} -alkoxycarbonyl group being attached either to the nitrogen in the 3- or 4-position;

20

R^2 is hydrogen, C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, C_4 - C_{10} -alkadienyl, C_1 - C_{10} -haloalkyl, C_3 - C_6 -cycloalkyl, C_8 - C_{14} -bicycloalkyl, phenyl, naphthyl, 5- or 6-membered heteroaryl or heterocyclic groups containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members;

25

R^3 is phenyl, C_3 - C_6 -cycloalkyl or 5- or 6-membered heteroaryl containing besides carbon atoms one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members;

30

R^4 is halogen, amino, C_1 - C_{10} -alkoxy, C_1 - C_{10} -haloalkoxy, C_1 - C_{10} -alkylamino or di- C_1 - C_{10} -alkylamino;

35

wherein the bent line indicates that the double Bond may be located between the 3- and 9- position or the 4- and 9-Position; and the zigzag line indicates that the groups connected may have the (E)- or (Z)-configuration;

40

R^1 to R^4 groups independently from one another may be unsubstituted or substituted by one to three groups R^a .

45

R^a halogen, nitro, cyano, hydroxy, C_1 - C_6 -alkyl, C_3 - C_6 -cycloalkyl, C_3 - C_6 -cycloalkenyl, C_1 - C_6 -haloalkyl, C_3 - C_6 -halocycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy, tri- C_1 - C_4 -alkylsilyl, phenyl, halo- or dihalo-phenyl or pyridyl;

2

It is an object of the present invention to provide fungicidal active compounds.

Moreover, the invention relates to processes for preparing these compounds, to compositions comprising them and to their use for controlling harmful fungi.

Fungicidal 7-amino-triazolopyrimidines are disclosed for example by US 5,593,996, WO-A 98/14608, FR-A 2,765,875 and WO-A 99/48893.

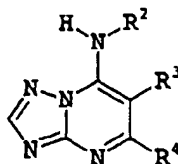
10

It is an object of the present invention to provide compounds having improved activity.

We have found that this object is achieved by the compounds defined at the outset. Furthermore, we have found processes for their preparation, compositions comprising them and methods for controlling animal pests and harmful fungi using the compounds I.

The present invention further provides a process for the preparation of a compound of formula I as defined above which comprises treating a compound of formula II

25



II

in which R² through R⁴ are as defined in claim 1;

with an alkylation agent of formula III

R¹-X

III

in which R¹ is as defined in formula I and X represents a nucleophilic exchangeable leaving group, preferably a halogen atom, in particular a bromine or iodine atom, in the presence of a weak base or a buffer system.

Compounds of formula II are known for example from US 5,593,996, WO 98/14608, FR-A 2,765,875 or WO-A 99/48893.

The reaction between the triazolopyrimidines of formula II, the weak base and the alkylating agent of formula III is preferably carried out in the presence of an inert solvent. Suitable solvents include ethers, such as dioxane, diethyl ether and tetrahydrofuran, halogenated hydrocarbons such as dichloromethane, amides, such as dimethylformamide or N-methylpyrrolidone and aro-

3

matic hydrocarbons, for example toluene or mixtures of these solvents.

The reaction is suitably carried out at a temperature in the range from -78°C to 100°C, the preferred reaction temperature is from 10°C to 80°C, particular at ambient temperature. Suitable weak bases include tertiary amines such as triethylamine or pyridine, metal carbonates such as sodium carbonate or carbonate or metal hydrogencarbonates such as sodium hydrogencarbonate or potassium hydrogencarbonate.

In the symbol definitions given in the formulae above, collective terms were used which generally represent the following substituents:

15

The term halogen atom may denote a bromine; iodine, chlorine or fluorine atom, and is especially a bromine, chlorine or fluorine atom, in particular a fluorine or chlorine atom.

- 20 The terms alkyl, alkenyl, alkynyl, alkadienyl, haloalkyl as used herein with respect to a radical or moiety refer to a straight or branched chain radical or moiety. Such radicals have up to 10, in particular up to 6 carbon atoms. Suitably an alkyl moiety has from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms. A preferred alkyl moiety is an ethyl or especially a methyl group.
- 25 Suitably an alkenyl moiety has from 2 to 6 carbon atoms. A preferred alkenyl moiety is allyl or especially a 2-methylallyl group. Suitably a haloalkyl moiety has from 1 to 6 fluorine atoms. A preferred haloalkyl moiety is the 2,2,2-trifluoroethyl
- 30 or 1,1,1-trifluoroprop-2-yl group.

The term heteroaryl, as used herein with respect to a radical or moiety refers to a heteroaryl group having 5 or 6 ring atoms selected from carbon, nitrogen, oxygen and sulfur, at least one of which being nitrogen, oxygen or sulfur, in particular pyridyl, pyrimidyl, pyrazolyl or thienyl.

The term cycloalkyl, as used herein with respect to a radical or moiety refers to a cycloalkyl group having 3 to 8 carbon atoms, preferably 5 to 7 carbon atoms, in particular cyclopentyl being optionally substituted by one or more halogen atoms, nitro, cyano, alkyl, preferably C₁-C₆-alkyl, alkoxy, preferably C₁-C₆-alkoxy.

45 The term heterocyclyl, as used herein with respect to a radical or moiety refers to a saturated heterocyclyl group having 5 or 6 ring atoms selected from carbon, nitrogen, oxygen and sulfur, at

4

least one of which being-nitrogen, oxygen or sulfur being optionally substituted by one or more halogen atoms, nitro, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy, in particular pyrrolidinyl, pyrazolidinyl, piperidinyl, piperazinyl or morpholin-4-yl.

5

The term trihydrocarbylsilyl, as used herein which respect to a radical or moiety refers to a silyl group which is substituted by three alkyl and/or phenyl groups. Most preferred are trimethylsilyl, triethylsilyl, tert.-butyldimethylsilyl and tert.-butyl-diphenylsilyl.

The invention especially relates to compounds of formula I in which any alkyl or haloalkyl part of the groups R¹, R², R³ or R⁴, which may be straight chained or branched, contains preferably 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any alkenyl, alkadienyl or alkynyl part of the substituents R¹ or R² contains preferably 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituent R¹ contains preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms. Any alkyl, alkenyl, alkadienyl or alkynyl group may be linear or branched. A 5- to 6- membered heterocyclic group may be any heterocyclic group with 5 to 6 ring atoms, interrupted by one or more heteroatoms selected from sulfur, nitrogen, and oxygen, preferably oxygen.

25

The invention especially relates to compounds of the general formula I in which R¹ represents a straight-chained or branched C₁-C₁₀-alkyl, in particular a straight-chained C₁-C₆-alkyl group, a C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl or a C₁-C₁₀-haloalkyl group.

The invention especially relates to compounds of the general formula I in which R² represents a straight-chained or branched C₁-C₁₀-alkyl, in particular a branched C₃-C₆-alkyl group, a C₃-C₈-cycloalkyl, a C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl, a C₁-C₁₀-haloalkyl or a phenyl group being optionally substituted by one to three halogen atoms or C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy groups.

Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.

45

5

With respect to their intended use, preference is given to compounds of formula I having the following substituents, where the preference is valid in each case on its own or in combination:

5

R¹ most preferably is a C₁-C₆-alkyl group.

Compounds of formula I are preferred wherein R¹ is in 3- or 4-position and denotes methyl, ethyl or n- or iso-propyl.

10

R² most preferably denotes a C₁-C₁₀-haloalkyl group, in particular a polyfluorinated alkyl group, most preferred a 2,2,2-trifluoroethyl, a 2-(1,1,1-trifluoropropyl) or a 2-(1,1,1-trifluorobutyl) group or an optionally substituted C₃-C₈-cycloalkyl group, preferably a cyclopentyl or cyclohexyl group.

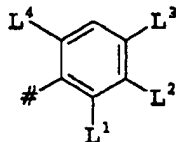
Compounds of formula I are preferred wherein R³ is phenyl optionally substituted by one or more fluorine and/or chlorine atoms and/or methoxy groups.

20

Compounds of formula I are particularly preferred in which R³ represents a phenyl group being substituted by 2 or 3 substituents. Most preferred at least one of these substituents is attached in the 2-position with respect to the point of attachment to the pyrimidine moiety. Such substituents preferably include a

Moreover, compounds of formula I are particularly preferred in which R³ is an optionally substituted phenyl group of formula

30



wherein # denotes the bond to the triazolopyrimidine ring and L¹ through L⁴ each independently are hydrogen, fluorine or chlorine or methoxy, in particular wherein L¹ is fluorine or chlorine, L² and L⁴ each independently are hydrogen or fluorine or chlorine, L³ is hydrogen or fluorine or chlorine or methoxy.

40

Compounds of formula I in which R⁴ represents a halogen atom, in particular a chlorine atom are particularly preferred.

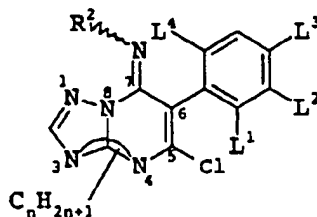
45

T02T90" 85267860

6

Most preferred are the compounds of formula IA

5



IA

in which R^2 has the meaning given for formula I, L^1 represents halogen and L^3 and L^4 each independently represent hydrogen, halogen or alkoxy, and n represents an integer from 1 to 10.

Especially preferred are following compounds of formula I:

- 15 N-[5-chloro-4-methyl-S-(2,4,6-trifluorophenyl)-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-(2,2,2-trifluoroethyl)-amine, N-[5-chloro-4-methyl-6-(2,4,6-trifluorophenyl)-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-cyclopentyl-amine, N-[5-chloro-4-methyl-6-(2,4,6-trifluorophenyl)-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-(1,1,1)-trifluoroprop-2-yl)-amine,
- 20 N-[5-chloro-4-methyl-6-(2,4,6-trifluorophenyl) 4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-isopropyl-amine, N-sec-butyl-N-[5-chloro-4-methyl-6-(2,4,6-trifluorophenyl)-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-amine,
- 25 N-bicyclo[2.2.1]hept-2-yl-N-(5-chloro-4-methyl-6-(2,4,6-trifluorophenyl)-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene)-amine, N-[5-chloro-6-(2-chloro-6-fluorophenyl)-4-methyl-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-cyclopentyl-amine,
- 30 N-[5-chloro-6-(2-chloro-6-fluorophenyl)-4-methyl-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-(2,2,2-trifluoroethyl)-amine, N-[5-chloro-6-(2-chloro-6-fluoro-phenyl)-4-methyl-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-(1,1,1-trifluoroprop-2-yl)-amine,
- 35 N-[5-chloro-6-(2-chloro-6-fluoro-phenyl)-4-methyl-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-isopropyl-amine, N-sec-butyl-N-[5-chloro-6-(2-chloro-6-fluorophenyl)-4-methyl-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-amine, N-bicyclo[2.2.1]hept-2-yl-N-[5-chloro-6-(2-chloro-6-fluorophenyl)-4-methyl-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-amine,
- 40 N-[5-chloro-6-(2,6-difluoro-4-methoxyphenyl)-4-methyl-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-(1,1,1-trifluoroprop-2-yl)-amine,
- 45 N-[5-chloro-6-(2,6-difluoro-4-methoxyphenyl)-4-methyl-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene]-N-(2,2,2-trifluoroethyl)-amine,

7

- N-[5-chloro-6-(2,6-difluoro-4-methoxyphenyl)-4-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene]-N-cyclopentylamine, N-(5-chloro-3-methyl-6-(2,4,6-trifluorophenyl)-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-(2,2,2-trifluoroethyl)-amine,
- 5 N-(5-chloro-3-methyl-6-(2,4,6-trifluorophenyl)-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-cyclopentylamine, N-[5-chloro-3-methyl-6-(2,4,6-trifluorophenyl)-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-(1,1,1-trifluoroprop-2-yl)-amine,
- 10 N-[5-chloro-3-methyl-6-(2,4,6-trifluorophenyl)-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-isopropylamine, N-sec-butyl-N-[5-chloro-3-methyl-6-(2,4,6-trifluorophenyl)-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-amine,
- 15 N-bicyclo[2.2.1]hept-2-yl-N-[5-chloro-3-methyl-6-(2,4,6-trifluorophenyl)-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-amine, N-(5-chloro-6-(2-chloro-6-fluorophenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-cyclopentylamine, N-[5-chloro-6-(2-chloro-6-fluorophenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-(2,2,2-trifluoroethyl)-amine,
- 20 N-[5-chloro-6-fluorophenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-(1,1,1-trifluoroprop-2-yl)-amine, N-[5-chloro-6-(2-chloro-6-fluorophenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-isopropylamine,
- 25 N-sec.-butyl-N-[5-chloro-6-(2-chloro-6-fluorophenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-amine, N-bicyclo[2.2.1]hept-2-yl-N-[5-chloro-6-(2-chloro-6-fluorophenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-amine,
- 30 N-[5-chloro-6-(2,6-difluoro-4-methoxyphenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-(1,1,1-trifluoroprop-2-yl)-amine, N-[5-chloro-6-(2,6-difluoro-4-methoxyphenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-(2,2,2-trifluoroethyl)-amine,
- 35 N-[5-chloro-6-(2,6-difluoro-4-methoxyphenyl)-3-methyl-3H-[1,2,4]triazolo[1,5-a]pyrimidin-7-ylidene)-N-cyclopentylamine.

The invention relates furthermore to a composition which consists of two compounds of formula I as defined hereinbefore, wherein

- (a) one compound of formula I wherein R¹ is attached in the 3 position; and
- 45 (b) one compound of formula I wherein R¹ is attached in the 4 position.

8

Due to excellent activity, the compounds of formula I may be used in cultivation of all plants where infection by phytopathogenic fungi is not desired, e.g. cereals, solanaceous crops, vegetables, legumes, apples, vine.

5

Moreover, the compounds I are suitable for controlling harmful fungi such as *Paecilomyces variotii* in the protection of materials (e.g. wood, paper, paint dispersions, fibers and tissues) and in the protection of stored products.

10

The compounds I are applied by treating the fungi, or the plants, seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application can be effected both before and after infection of the materials, plants or seeds by the fungi.

When used in crop protection, the rates of application are from 0.01 to 2.0 kg of active ingredient per ha, depending on the nature of the effect desired.

20

In the treatment of seed, amounts of active ingredient of from 0.001 to 0.1 g, preferably 0.01 to 0.05 g, are generally required per kilogram of seed.

25 When used in the protection of materials or stored products, the rate of application of active ingredient depends on the nature of the field of application and on the effect desired. Rates of application conventionally used in the protection of materials are, for example, from 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of
30 active ingredient per cubic meter of material treated.

The invention further provides a fungicidal composition which comprises an active ingredient, which is at least one compound of formula I as defined above, and one or more carriers.

35

A method of making such a composition is also provided which comprises bringing a compound of formula I as defined above into association with the carrier(s). Such a composition may contain a single active ingredient or a mixture of several active ingredients of the present invention. It is also envisaged that different isomers or mixtures of isomers may have different levels or spectra of activity and thus compositions may comprise individual isomers or mixtures of isomers.

45 A composition according to the invention preferably contains from 0.5% to 95% by weight (w/w) of active ingredient.

09879258-061201

9

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed, soil, or water in which a plant grows, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including material which is normally a gas but which has been compressed to form a liquid.

The compositions may be manufactured into e.g. emulsion concentrates, solutions, oil in water emulsions, wettable powders, soluble powders, suspension concentrates, dusts, granules, water dispersible granules, micro-capsules, gels, tablets and other formulation types by well-established procedures. These procedures include intensive mixing and/or milling of the active ingredients with other substances, such as fillers, solvents, solid carriers, surface active compounds (surfactants), and optionally solid and/or liquid auxiliaries and/or adjuvants. The form of application such as spraying, atomizing, dispersing or pouring may be Chosen like the compositions according to the desired objectives and the given circumstances.

Solvents may be aromatic hydrocarbons, e.g. Solvesso® 200, substituted naphthalenes, phthalic acid esters, such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, or γ -butyrolactone, higher alkyl pyrrolidones, e.g. n-octylpyrrolidone or cyclohexylpyrrolidone, epoxidized plant oil esters, e.g. methylated coconut or soybean oil ester and water. Mixtures of different liquids are often suitable.

Solid carriers, which may be used for dusts, wettable powders, water dispersible granules, or granules, may be mineral fillers, such as calcite, talc, kaolin, montmorillonite or attapulgite. The physical properties may be improved by addition of highly dispersed silica gel or polymers. Carriers for granules may be porous material, e.g. pumice, kaolin, sepiolite, bentonite; non-sorptive carriers may be calcite or sand.

Additionally, a multitude of pre-granulated inorganic or organic materials may be used, such as dolomite or crushed plant residues.

45

10

Pesticidal compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surfactant facilitates this process of dilution. Thus, preferably at least one carrier in a composition according to the invention is a surfactant. For example, the composition may contain at two or more carriers, at least one of which is a surfactant.

10 Surfactants may be nonionic, anionic, cationic or zwitterionic substances with good dispersing, emulsifying and wetting properties depending on the nature of the compound according to general formula I to be formulated. Surfactants may also mean mixtures of individual surfactants.

15 The compositions of the invention may for example be formulated as wettable powders, water dispersible granules, dusts, granules, tablets, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols.

20 Wettable powders usually contain 5 to 90% w/w of active ingredient and usually contain in addition to solid inert carrier, 3 to 10% w/w of dispersing and wetting agents and, where necessary, 0 to 10% w/w of stabilizer(s) and/or other additives such as penetrants or stickers.

Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and may be diluted in the field with further solid carrier to give a composition usually containing 0.5 to 10% w/w of active ingredient.

Water dispersible granules and granules are usually prepared to have a size between 0.15 mm and 2.0 mm and may be manufactured by a variety of techniques. Generally, these types of granules will contain 0.5 to 90% w/w active ingredient and 0 to 20% w/w of additives such as stabilizer, surfactants, slow release modifiers and binding agents.

40 The so-called "dry flowables" consist of relatively small granules having a relatively high concentration of active ingredient.

Emulsifiable concentrates usually contain, in addition to a solvent or a mixture of solvents, 1 to 80% w/v active ingredient, 2 to 20% w/v emulsifiers and 0 to 20% w/v of other additives such as stabilizers, penetrants and corrosion inhibitors.

11

Suspension concentrates are usually milled so as to obtain a stable, nonsedimenting flowable product and usually contain 5 to 75% w/v active ingredient, 0.5 to 15% w/v of dispersing agents, 0.1 to 10% w/v of suspending agents such as protective colloids and thixotropic agents, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation and crystalization or as anti-freeze agents for water.

Aqueous dispersions and emulsions, for example compositions obtained by diluting the formulated product according to the invention with water, also lie within the scope of the invention.

Of particular interest in enhancing the duration of the protective activity of the compounds of this invention is the use of a carrier which will provide slow release of the pesticidal compounds into the environment of a plant which is to be protected.

The biological activity of the active ingredient can also be increased by including an adjuvant in the spray dilution. An adjuvant is defined here as a substance which can increase the biological activity of an active ingredient but is not itself significantly biologically active. The adjuvant can either be included in the formulation as a coformulant or carrier, or can be added to the spray tank together with the formulation containing the active ingredient.

As a commodity the compositions may preferably be in a concentrated form whereas the end user generally employs diluted compositions. The compositions may be diluted to a concentration down to 0.001 % of active ingredient. The doses usually are in the range from 0.01 to 10 kg a.i./ha.

40

45

12

Examples of formulations according to the invention are:

Emulsion Concentrate (EC)

5	Active Ingredient	Compound of Example 1	30.-% (w/v)
10	Emulsifier(s)	Atlox [®] 4856B/Atlox [®] 4858B ¹⁾ (mixture containing calcium alkyl arylsulfonate, fatty alcohol ethoxylates and light aromatics /mixture containing calcium alkyl aryl sulfonate, fatty alcohol ethoxylates and light aromatics)	5 % (w/v)
15	Solvent	Shellsol [®] A ²⁾ (mixture of C ₉ -C ₁₀ aromatic hydrocarbons)	to 1000 ml

Suspension Concentrate (SC)

	Active Ingredient	Compound of Example 1	50 % (w/v)
20	Dispersing agent	Soprophor [®] FL ³⁾ (polyoxyethylene polyaryl phenyl etherphosphate amine salt)	3 % (w/v)
	Antifoaming agent	Rhodorsil [®] 422 ³⁾ (nonionic aqueous emulsion of polydimethylsiloxanes)	0.2 % (w/v)
25	Structure agent	Kelzan [®] S ⁴⁾ (Xanthan gum)	0.2 % (w/v)
	Antifreezing agent	Propylene glycol	5 % (w/v)
30	Biocidal agent	Proxel [®] 5) (aqueous dipropylene glycol solution containing 20% 1,2-beniso-thiazolin-3-one)	0.1 % (w/v)
	Water		to 1000 ml

35 Wettable Powder (WP)

	Active Ingredient	Compound of Example 4	60 % (w/w)
	Wetting agent	Atlox [®] 4995 ¹⁾ (polyoxyethylene alkyl ether)	2 % (w/w)
40	Dispersing agent	Witcosperse [®] D-60 ⁶⁾ (mixture of sodium salts of condensed naphthalene sulfonic acid and alkylaryl polyoxy acetates)	3 % (w/w)
	Carrier / Filler	Carrier / Filler	35 % (w/w)

45

13

Water Dispersible Granules (WG)

	Active Ingredient	Compound of Example 12	50 % (w/w)
5	Dispersing / Binding agent	Witcosperse [®] D-450 ⁶⁾ (mixture of sodium salts of condensed naphthalene sulfonic acid and alkyl sulfonates)	8 % (w/w)
	Wetting agent	Morwet [®] EFW ⁶⁾ (formaldehyde condensation product)	2 % (w/w)
10	Antifouling agent	Rhodorsil [®] EP 6703 ³⁾ (encapsulated silicone)	1 % (w/w)
	Disintegrant	Agrimer [®] ATF ⁷⁾ (cross-linked homopolymer of N-vinyl-2-pyrrolidone)	2 % (w/w)
15	Carrier / Filler	Carrier / Filler	35 % (w/w)

- 1) commercially available from ICI Surfactants
 2) commercially available from Deutsche Shell AG
 20 3) commercially available from Rhône-Poulenc
 4) commercially available from Kelco Co.
 5) commercially available from Zeneca
 6) commercially available from Witco
 7) commercially available from International Speciality Products

25

The compositions of this invention can be applied to the plants or their environment simultaneous with or in succession with other active substances. These other active substances can be either fertilisers, agents which donate trace elements or other
 30 preparations which influence plant growth. However, they can also be selective herbicides, insecticides, fungicides, bactericides, nematocides, algicides, molluscicides, rodenticides, virucides, compounds inducing resistance into plants, biological control agents such as viruses, bacteria, nematodes, fungi and other micro-
 35 organisms, repellents of birds and animals, and plant growth regulators, or mixtures of several of these preparations, if appropriate together with other carrier substances conventionally used in the art of formulation, surfaceness or other additives which promote application.

40

The other fungicidal compound can be, for example, one which is also capable of combating diseases of cereals (e.g. wheat) such as those caused by *Erysiphe*, *Puccinia*, *Septoria*, *Gibberelia* and *Helminthosporium* spp., seed and soil borne diseases and downy and
 45 powdery mildews on vines, early and late blight on solanaceous crops, and powdery mildew and scab on apples etc. These mixtures

14

of fungicides can have a broader spectrum of activity than the compound of general formula I alone.

Examples of the other fungicidal compounds are anilazine, azoxy-
 5 strobil, benalaxyl, benomyl, binapacryl, bitertanol, blastidicidin
 S, Bordeaux mixture, bromuconazole, bupirimate, captafol, captan,
 carbendazim, carboxin, carpropamid, chlorbenzthiazon, chloro-
 thalonil, chlozolinate, copper-containing compounds such as
 copper oxychloride and copper sulfate, cyazofamide, cyclohexi-
 10 mide, cymoxanil, cypofuram, cyproconazole, cyprodinil, dichlo-
 fluamid, dichlone, dichloran, diclobutrazol, diclocymet, diclome-
 zine, diethofencarb, difenoconazole, diflumetoxim, dimethirimol,
 dimethomorph, diniconazole, dinocap, ditalimfos, dithianon, dode-
 morph, dodine, edifenphos, epoxiconazole, etaconazole, ethirimol,
 15 etridiazole, famoxadone, fenapanil, fenamidone, fenarimol, fenbu-
 conazole, fenfuram, fenhexamid, fenoxanil, fenciclonil, fenpropi-
 din, fenpropimorph, fentin, fentin acetate, fentin hydroxide,
 ferimzone, fluazinam, fludioxonil, flumetover, fluquinconazole,
 flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fose-
 20 tyl-aluminium, fuberidazole, furalaxyl, furametpyr, guazatine,
 hexaconazole, imazalil, iminoctadine, ipconazole, iprodione, iso-
 prothiolane, iprovalicarb, kasugamycin, KH-7281, kitazin P, kre-
 soxim-methyl, mancozeb, maneb, mepanipyrim, mepronil, metalaxyl,
 metconazole, methfuroxam, MON 65500, myclobutanil, neoasozin,
 25 nicket dimethyldithiocarbamate, nitrothalisopropyl, nuarimol,
 ofurace, organo mercury compounds, oxadixyl, oxycarboxin, pencona-
 zole, pencycuron, phenazineoxide, phthalide, picoxystrobin, poly-
 oxin D, polyram, probenazole, prochloraz, procymidione, propamo-
 carb, propiconazole, propineb, pyraclostrobin, pyrazophos, pyri-
 30 fenox, pyrimethanil, pyroquilon, pyroxyfur, quinomethionate, qui-
 noxyfen, quintozone, spiroxamine, SSF-126, SSF-129, streptomycin,
 sulfur, tebuconazole, tecloftalame, tecnazene, tetraconazole,
 thiabendazole, thifluzamide, thiophanate-methyl, thiram, tolclo-
 fosmethyl, tolylfluanid, triadimefon, triadimenol, triazbutyl,
 35 triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumi-
 zole, triforine, triticonazole, validamycin A, vinclozolin,
 XRD-563, zarilamid, zineb, ziram.

In addition, the co-formulations according to the invention may
 40 contain at least one compound of formula I and any of the follow-
 ing contain at least one compound of formula I and any of the
 following classes of biological control agents such as viruses,
 bacteria, nematodes, fungi, and other microorganisms which are
 suitable to control insects, weeds or plant diseases or to induce
 45 host resistance in the plants. Examples of such biological con-
 trol agents are: *Bacillus thuringiensis*, *Verficillium lecanii*,
Autographa californica NPV, *Beauveria bassiana*, *Ampelomyces*

15

quisqualis, Bacillus subtilis, Pseudomonas chlororaphis, Pseudomonas fluorescens, Streptomyces griseoviridis and Trichoderma harzianum.

- 5 Moreover, the co-formulations according to the invention may contain at least one compound of formula I and a chemical agent that induces the systemic acquired resistance in plants such as for example isonicotinic acid or derivatives thereof, 2,2-dichloro-3,3-dimethylcyclopropanecarboxylic acid or BION.

10

The compounds of general formula I can be mixed with soil, pest or other rooting media for the protection of the plants against seed-borne, soil-borne or foliar fungal diseases.

- 15 The invention still further provides the use as a fungicide of a compound of the general formula I as defined above or a composition as defined above, and a method for combating fungus at a locus, which comprises treating the locus, which may be for example plants subject to or subjected to fungal attack, seeds of
20 such plants or the medium in which such plants are growing or are to be grown, with such a compound or composition.

The present invention is of wide applicability in the protection of crop and ornamental plants against fungal attack. Typical

- 25 crops which may be protected include vines, grain crops such as wheat and barley, rice, sugar beet, top fruit, peanuts, potatoes, vegetables and tomatoes. The duration of the protection is normally dependent on the individual compound selected, and also a variety of external factors, such as climate, whose impact is
30 normally mitigated by the use of a suitable formulation.

Synthesis Examples

- With due modification of the starting compounds, the protocols
35 shown in the synthesis examples below were used for obtaining further compounds I. The resulting compounds, together with physical data, are listed in the Table which follows.

40

45

16

- Example 1 Preparation of N-(5-chloro-4-methyl-6-(2,4,6-trifluorophenyl)-4H[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene)-N-(2,2,2-trifluoroethyl)-amine 1A and N-[5-chloro-3-methyl-6-(2,4,6-trifluorophenyl)-4H-[1,2,4]triazolo[1,5- α]pyrimidin-7-ylidene)-N-(2,2,2-trifluoroethyl)-amine 1B

A mixture of 5-chloro-6-(2,4,6-trifluorophenyl)-7-(1,1,1-trifluoroprop-2-ylamino)-triazolo[1.5- α]pyrimidine (2.5 g, 6.3 mmol, prepared according to WO-A 98/46608), dimethylformamide (15ml), potassium hydrogencarbonate (10 g) and methyl iodide was stirred at ambient temperature for 45 minutes. The reaction mixture was poured into water (400 ml) and extracted with diethylether twice (300 ml). The organic Phase was separated, dried with anhydrous sodium sulphate and filtered. The filtrate was evaporated under reduced pressure and purified by flash chromatography to yield 2 g of the product as a mixture of 1A and 1B. The regioisomers were separated by column chromatography to yield

- 20 1A: 0.8 g, m.p. 112-120 °C
1B: 0.7 g, m.p. 165-167 °C

Table I

Ex.	R ¹	R ²	L ¹	L ³	L ⁴	melting point (°C)
2	4-n-propyl	1,1,1-trifluoroprop-2-yl	F	F	F	105-109
3	4-ethyl	1,1,1-trifluoroprop-2-yl	F	F	F	95
4	4-n-propyl	1,1,1-trifluoroprop-2-yl	F	OCH ₃	F	95
5	4-methyl	1,1,1-trifluoroprop-2-yl	F	H	F	147-151
6	4-methyl	1,1,1-trifluoroprop-2-yl	Cl	H	H	151-160
7	4-methyl	1,1,1-trifluoroprop-2-yl	F	F	H	110-114
8	4-methyl	2,2,2-trifluoroethyl	F	F	F	125
9	3-n-propyl	1,1,1-trifluoroprop-2-yl	F	OC ₃ H ₇	F	155
10	3-ethyl	1,1,1-trifluoroprop-2-yl	F	F	F	138
11	3-n-propyl	1,1,1-trifluoroprop-2-yl	F	F	F	127
12	3-n-propyl	1,1,1-trifluoroprop-2-yl	F	OCH ₃	F	169
13	3-methyl	1,1,1-trifluoroprop-2-yl	F	OCH ₃	F	176-180
14	3-methyl	1,1,1-trifluoroprop-2-yl	F	H	F	172-175
15	3-methyl	1,1,1-trifluoroprop-2-yl	Cl	H	H	153-162
16	3-methyl	1,1,1-trifluoroprop-2-yl	F	F	H	159-162
17	4-methyl	2,2,2-trifluoroethyl	F	F	F	137

17

Biological investigations

A Evaluation of In Vivo Fungicidal Activity of Test Compounds

5 Test compounds are dissolved in acetone and diluted with deionized water (95 parts water to 5 parts acetone) containing 0.05% TWEEN 20®, a polyoxyethylene sorbitan monolaurate surfactant TWEEN 20®, a polyoxyethylene sorbitan monolaurate surfactant 200, 50 and 12.5 ppm.

10 The plants are sprayed with the test solutions, dried and inoculated with fungi later the same day. When disease symptom development is optimal, the plants are rated for disease control according to the rating scale shown below. Each test

15 contains inoculated treated plants, inoculated untreated plants and inoculated plants treated with reference fungicides. The data obtained are shown in Table II.

RATING SCALE

20	Rating	Range % Control
	0	0
	1	1-14
25	2	15-29
	3	30-44
	4	45-59
	5	60-74
	6	75-89
30	7	90-95
	8	96-99
	9	100
	t	no evaluation possible

35 TARGETS

	Abbreviation	Disease	Pathogen
	AS	Apple Scab	Venturia inaequalis
	GDM	Grape downy mildew	Plasmopara viticola
40	PB	Pepper Botrytis	Botrytis cinera
	RB	Rice Blast	Pyricularia grisea f. sp. oryzae
	SBC	Sugar Beet Cercospora	Cercospora beticola
45	TEB	Tomato early blight	Alternaria solani
	WPM	Wheat powdery mildew	Blumeria graminis

18

B Evaluation of in vitro fungicidal activity

Test compounds are dissolved in acetone to give concentrations of 25, 10 and 1 ppm and are added to individual cell walls (24-cell-well plates, Corning), which were previously filled with a suspension of ground plates, Corning), which were previously filled with a suspension of ground fungal mycelium in a chemically defined growth medium. After 3-7 days of incubation, inhibition of mycelial growth is recorded using the following scale: The data obtained are shown in Table II.

RATING SCALE

15

Rating

Degree of Inhibition

0

None

3

slight

20

5

moderate

7

severe

9

complete

TARGET

25

Symbol

Disease

Pathogen

PSDCHE

Cereal eye spot

Pseudocercospora herpotrichoides

30

PYTHUL

Fruit rot

Pythium ultimum

RHIZSO

Rice sheath blight

Rhizoctonia solani

Table II

Ex.	Dose [ppm]	AS	GDM	PB	RB	SBC	TEB	WPM	PSDCH	PYTHU	RHIZSO
1A	200	9	4	0	6	8	3	8			
1A	50	6	6	5	0	6	0	7			
1A	12,5	0	5	0	0	0	0	0			
1A	25								0	0	7
1A	10								0	0	7
1A	1								0	0	5
1B	200	5	7	6	5	6	4	0			
1B	50	4	0	0	0	6	2	0			

19

	Ex.	D se [ppm]	AS	GDM	PB	RB	SBC	TEB	MPM	PSDCH	PYTHU	RHIZO
5	1B	12,5	4	0	0	0	0	0	0			
	1B	25								3	5	5
	1B	10								1	1	5
	1B	1								0	0	5
10	2	200	5	1	1	0	3	0	0			
	2	50	0	2	1	0	0	0	0			
	2	12,5	0	4	1	0	0	0	0			
	3	200	6	4	0	5	0	0	3			
15	3	50	0	4	0	0	0	3	0			
	3	12,5	0	0	2	0	0	3	0			
	3	25								1	0	5
	3	10								1	0	5
20	3	1								0	0	3
	4	50	0	0	0	0	0	0	0			
	4	12,5	0	0	0	0	0	0	0			
	4	3,1	0	4	0	0	0	3	0			
25	5	200	0	5	1	0		0	6			
	5	50	0	6	0	0		0	3			
	5	12,5	0	6	0	0		0	0			
	6	200	5	7	0	5		0	5			
30	6	50	0	0	0	0		0	0			
	6	12,5	0	0	0	0		0	0			
	6	25								0	0	0
	6	10								1	0	0
35	6	1								0	0	0
	7	200	6	8	0	4		0	6			
	7	50	0	0	0	0		0	4			
	7	12,5	0	0	2	0		0	0			
40	7	25								0	0	5
	7	10								1	0	5
	7	1								0	0	5
	8	200	5	5	0	4		0	7			
45	8	50	0	4	0	0		0	4			
	8	12,5	0	5	0	0		2	2			
	8	25								0	0	7
	8	10								0	0	7
	8	1								0	0	7

Sub
A2

T02F90"85264860

20

	Ex.	Dose [ppm]	AS	ODM	PB	RB	SBC	TEB	WPM	PSDCH	PYTHU	RHIZO
5	9	200	6	3	2	4	8	9	7			
	9	50	6	3	1	3	8	8	6			
	9	12,5	0	5	2	0	8	6	2			
	9	25								5	0	7
10	9	10								3	0	7
	9	1								3	0	7
	10	200	6	0	0	6	6	5	0			
	10	50	0	0	0	4	6	4	0			
15	10	12,5	0	0	4	0	3	0	0			
	10	25								0	5	5
	10	10								0	3	5
	10	1								0	0	0
20	11	200	7	3	0	4	3	0	0			
	11	50	6	0	0	3	0	0	0			
	11	12,5	0	0	0	0	0	0	0			
	11	25								0	1	0
25	11	10								0	1	0
	11	1								0	0	0
	12	200	0	0	0	0	0	0	0			
	12	50	0	0	0	0	0	0	0			
30	12	12,5	0	0	0	0	0	0	0			
	13	200	0	0	0	0		0	5			
	13	50	0	0	0	0		0	3			
	13	12,5	0	0	0	0		0	0			
35	14	200	6	7	0	0		0	0			
	14	50	0	4	0	0		0	0			
	14	12,5	0	0	0	0		0	0			
	15	200	0	6	2	0		0	3			
40	15	50	0	4	0	0		0	0			
	15	12,5	0	2	0	0		0	0			
	15	25								0	0	3
	15	10								0	0	0
45	15	1								0	0	0
	16	200	6	7	0	0		0	0			
	16	50	5	5	0	0		0	0			
	16	12,5	0		0	0		0	0			
	16	25								0	7	7

Sub
A2

T02T90" 85262860

21

Sub
A2

	Ex.	Dose (ppm)	AS	GDM	PB	RB	SBC	TEB	WPM	PSDCH	PYTHU	RHIZSO
5	16	10								0	5	7
	16	1								0	0	5
	17	200	6	5	0	4		0	6			
10	17	50	2	0	0	3		0	2			
	17	12,5	0	0	0	0		0	0			
	17	25								3	7	7
	17	10								1	5	7
	17	1								0	0	7

15

20

25

30

35

40

45

T02T90" 85262860